

L4 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2010 ACS on STN  
AN 1992:84369 CAPLUS  
DN 116:84369  
OREF 116:14391a,14394a  
ED Entered STN: 06 Mar 1992  
TI Preparation of bifunctional (meth)acrylate esters  
IN Yamamoto, Masanobu; Nishikawa, Masaru; Matsumoto, Keizo  
PA Arakawa Chemical Industries, Ltd., Japan  
SO Jpn. Kokai Tokkyo Koho, 6 pp.  
CODEN: JKXXAF

DT Patent  
LA Japanese  
CC 35-2 (Chemistry of Synthetic High Polymers)  
Section cross-reference(s): 23

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	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 03236349	A	19911022	JP 1990-32999	19900213 <-
PRAI	JP 1990-32999			19900213	

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 03236349	IPCI	C07C0069-54 [ICM,5]; C07C0069-00 [ICM,5,C*]; B01J0031-02 [ICS,5]; C07C0067-08 [ICS,5]; C07C0067-00 [ICS,5,C*]; B01J0027-02 [ICA,5]; B01J0027-12 [ICA,5]; B01J0027-06 [ICA,5,C*]; C07B0061-00 [ICA,5] IPCR B01J0027-02 [I,C*]; B01J0027-02 [I,A]; B01J0027-06 [I,C*]; B01J0027-12 [I,A]; B01J0031-02 [I,C*]; B01J0031-02 [I,A]; C07B0061-00 [I,C*]; C07B0061-00 [I,A]; C07C0067-00 [I,C*]; C07C0067-08 [I,A]; C07C0069-00 [I,C*]; C07C0069-54 [I,A]

OS MARPAT 116:84369

AB The title esters, with low irritability to skin, are prepared from C36 hydrogenated dimer acid diols (I). Thus, heating I (KX 500) 974.6, acrylic acid 3254, PhOMe 1.95, p-MeC6H4SO3H 65, and cyclohexane 520 g at 90° for 5 h gave a pale yellow liq ester. Photopolymn. of this ester gave films with elongation 13.6% and tensile strength 28.7 kg/cm2. ST dimer acid diol methacrylate; acrylate dimer acid diol; polymn photochem diol methacrylate

IT 79-10-7DP, Acrylic acid, esters with hydrogenated dimer acid diols  
79-41-4DP, Methacrylic acid, esters with hydrogenated dimer acid diols  
RL: PREP (Preparation)  
(preparation of)

RN 79-10-7DP

RN 79-41-4DP

L4 ANSWER 2 OF 3 WPIX COPYRIGHT 2010 THOMSON REUTERS on STN  
AN 1991-350873 [199148] WPIX

DNC C1991-151422 [199321]

TI Difunctional (meth)acrylic acid ester - prepared by esterification of dimer-diol, dimer of higher unsatd. fatty acid and (meth)acrylic acid

DC A41; E17; G02

IN MATSUMOTO K; NISHIKAWA M; YAMAMOTO M  
PA (ARAK-C) ARAKAWA KAGAKU KOGYO KK

CYC 1

PI JP 03236349 A 19911022 (199148)\* JA <-  
ADT JP 03236349 A JP 1990-32999 19900213

PRAI JP 1990-32999 19900213  
IPCR B01J0027-02 [I,A]; B01J0027-02 [I,C]; B01J0027-06 [I,C]; B01J0027-12 [I,A]; B01J0031-02 [I,A]; B01J0031-02 [I,C]; C07B0061-00 [I,A]; C07B0061-00 [I,C]; C07C0067-00 [I,C]; C07C0067-08 [I,A]; C07C0069-00 [I,C]; C07C0069-54 [I,A]

FCL B01J0027-02; B01J0027-12; B01J0031-02 103; C07B0061-00 300; C07C0067-08;

C07C0069-54 Z  
FTRM 4G069; 4H006; 4H039; 4H006/AA01; 4G069/AA02; 4H006/AA02; 4G069/AA06;  
4H006/AB46; 4H006/AB84; 4H006/AC48; 4G069/BA21.B; 4G069/BE22.B;  
4H039/CA66; 4G069/CB25; 4G069/CB75; 4H039/CD10; 4H039/CD30; 4H006/KA06;  
4H006/KE20

AB JP 03236349 A UPAB: 20050502  
A difunctional (meth)acrylic acid ester is prepared by esterifying a dimer diol obtd. by hydrogenation of 36C dimeric acid, dimer of higher unsatd. fatty acid, and (meth)acrylic acid.  
USE/ADVANTAGE - Provides difunctional (meth)acrylic acid esters with high polymerisation reactivity, less odour and less skin irritability easily copolymerising with unsatd. monomers and resins with unsatd. gps. in the presence of heat, UV light, ionisation radiation and radical polymerisation initiators useful for overprint varnishes, prim. coats for optical fibres, overcoats for plastics and metals, inks and paints and their mfg. method. - In an example, a mixture of 974.6g dimer diol, 325.4g 98% acrylic acid, 1.95g methoxyphenol, 65.0g p-toluenesulphonic acid and 520.0g cyclohexane is heated to 90 deg.C under stirring with air being introduced, esterified for 5 hours at the temperature under stirring with 70.6g generated water being removed, cooled and mixed with 700g toluene. The mixed solution is neutralised with 280.2g 20% NaOH aqueous solution, the water layer is removed. The organic layer is washed with three 600g portions of deionised water, into the layer, is added 0.464g methoxyphenol from the mixture, is distilled off the solvent under reduced pressure to give 1106.5g ester with a specific gravity of 0.9922, a viscosity at 25 deg.C of 120 cps and an acid values of 0.2 mgKOH/g. @6pp Dwg.No.0/0)

MC CPI: A01-C01; E10-G02B; G02-A02C4; G02-A04A  
AN 1991-350873 [199148] WPIX  
DNC C1991-151422 [199321]  
TI Difunctional (meth)acrylic acid ester - prepared by esterification of dimer-diol, dimer of higher unsatd. fatty acid and (meth)acrylic acid  
DC A41; E17; G02  
IN MATSUMOTO K; NISHIKAWA M; YAMAMOTO M  
PA (ARAK-C) ARAKAWA KAGAKU KOGYO KK  
CYC 1  
PI JP 03236349 A 19911022 (199148)\* JA <--  
ADT JP 03236349 A JP 1990-32999 19900213  
PRAI JP 1990-32999 19900213  
IPCR B01J0027-02 [I,A]; B01J0027-02 [I,C]; B01J0027-06 [I,C]; B01J0027-12 [I,A]; B01J0031-02 [I,A]; B01J0031-02 [I,C]; C07B0061-00 [I,A]; C07B0061-00 [I,C]; C07C0067-00 [I,C]; C07C0067-08 [I,A]; C07C0069-00 [I,C]; C07C0069-54 [I,A]  
PCL B01J0027-02; B01J0027-12; B01J0031-02 103; C07B0061-00 300; C07C0067-08; C07C0069-54 Z  
FTRM 4G069; 4H006; 4H039; 4H006/AA01; 4G069/AA02; 4H006/AA02; 4G069/AA06;  
4H006/AB46; 4H006/AB84; 4H006/AC48; 4G069/BA21.B; 4G069/BE22.B;  
4H039/CA66; 4G069/CB25; 4G069/CB75; 4H039/CD10; 4H039/CD30; 4H006/KA06;  
4H006/KE20

AB JP 03236349 A UPAB: 20050502  
A difunctional (meth)acrylic acid ester is prepared by esterifying a dimer diol obtd. by hydrogenation of 36C dimeric acid, dimer of higher unsatd. fatty acid, and (meth)acrylic acid.  
USE/ADVANTAGE - Provides difunctional (meth)acrylic acid esters with high polymerisation reactivity, less odour and less skin irritability easily copolymerising with unsatd. monomers and resins with unsatd. gps. in the presence of heat, UV light, ionisation radiation and radical polymerisation initiators useful for overprint varnishes, prim. coats for optical fibres, overcoats for plastics and metals, inks and paints and their mfg. method. - In an example, a mixture of 974.6g dimer diol, 325.4g 98% acrylic acid, 1.95g methoxyphenol, 65.0g p-toluenesulphonic acid and 520.0g cyclohexane is heated to 90 deg.C under stirring with air being introduced, esterified for 5 hours at the temperature under stirring with 70.6g generated water being removed, cooled and mixed with 700g toluene. The

mixed solution is neutralised with 280.2g 20% NaOH aqueous solution, the water layer

is removed. The organic layer is washed with three 600g portions of deionised water, into the layer, is added 0.464g methoxyphenol from the mixture, is distilled off the solvent under reduced pressure to give 1106.5g ester with a specific gravity of 0.9922, a viscosity at 25 deg.C of 120 cps and an acid values of 0.2 mgKOH/g. @{6pp Dwg.No.0/0}

FS CPI

MC CPI: A01-C01; E10-G02B; G02-A02C4; G02-A04A

L4 ANSWER 3 OF 3 JAPIO (C) 2010 JPO on STN

AN 1991-236349 JAPIO

TI BIFUNCTIONAL (METH)ACRYLIC ACID ESTER AND ITS PRODUCTION

IN YAMAMOTO MASANOBU; NISHIKAWA MASARU; MATSUMOTO KEIZO

PA ARAKAWA CHEM IND CO LTD

PI JP 03236349 A 1991022 Heisei

AI JP 1990-32999 (JP02032999 Heisei) 19900213

PRAI JP 1990-32999 19900213

SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 1991

IC ICM C07C069-54

ICS B01J031-02; C07C067-08

ICA B01J027-02; B01J027-12; C07B061-00

AB NEW MATERIAL: The bifunctional (meth)acrylic acid ester produced by esterifying acrylic acid or methacrylic acid with a dimer diol obtained by hydrogenating a 36C dimer acid which is a dimer of a higher unsaturated fatty acid.

USE: Useful as a polyfunctional monomer, reactive diluent, etc., having excellent reactivity and reducibility and remarkably decreased skin irritation.

PREPARATION: The objective bifunctional (meth)acrylic acid ester can be produced by esterifying acrylic acid or methacrylic acid with a dimer diol obtained by hydrogenating a 36C dimer acid which is a dimer of a higher unsaturated fatty acid. The dimer diol is especially preferably a compound of formula I ( $R<SB>_1</SB>$  and  $R<SB>_2</SB>$  are alkyl; the sum of n, m and the carbon numbers of  $R<SB>_1</SB>$ ,  $R<SB>_2</SB>$  is 30) and/or formula II ( $R<SB>_3</SB>$  and  $R<SB>_4</SB>$  are alkyl; the sum of q, r and the carbon numbers of  $R<SB>_3</SB>$ ,  $R<SB>_4</SB>$  is 34).

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PTO 10-4189

CC=JP  
DATE=19911022  
KIND=A  
PN=03236349

BIFUNCTIONAL (METH) ACRYLIC ESTER AND THE MANUFACTURING  
METHOD THEREOF

[二官能性(メタ)アクリル酸エステルおよびその製造法]

MASANOBU YAMAMOTO, ET AL.

UNITED STATES PATENT AND TRADEMARK OFFICE  
WASHINGTON, D.C. JUNE 2010  
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C 07 C 67/08  
// B 01 J 27/02  
27/12  
C 07 B 61/00

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PRIORITY NUMBER (31): N/A

PRIORITY DATE (32): N/A

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APPLICANT(S) (71): ARAKAWA CHEMICAL  
INDUSTRIES, LTD.

DESIGNATED CONTRACTING STATES (81): N/A

TITLE (54): BIFUNCTIONAL  
(METH)ACRYLIC ESTER  
AND THE MANUFACTURING  
METHOD THEREOF

FOREIGN TITLE [54A]: 二官能性(メタ)アクリル酸  
エステルおよびその製造法

SPECIFICATION

1. Title of the Invention

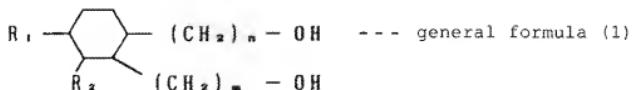
Bifunctional (Meth)acrylic Ester and the Manufacturing Method Thereof

2. Scope of Patent Claims

1) Bifunctional (meth)acrylic ester, comprising dimer diol, manufactured by hydrogenating C<sub>36</sub> Dimer acid that is a dimer of high unsaturated fatty acid, and acrylic/methacrylic acid, both of which are esterified.

2) A manufacturing method for bifunctional (meth)acrylic ester, which is manufactured by esterifying both dimer diol, manufactured by hydrogenating C<sub>36</sub> Dimer acid that is a dimer of high unsaturated fatty acid, and acrylic/methacrylic acid.

3) The manufacturing method, according to Claim 1) or 2), wherein the said dimer diol is a compound of the following general formula (1) and/or general formula (2).



(in the general formula (1), both R<sub>1</sub> and R<sub>2</sub> are alkyl groups and represent that a condition that a total of each number of carbons contained in R<sub>1</sub> and R<sub>2</sub>, and n and m is 28 is satisfied. Moreover, in the general formula (2), both R<sub>3</sub> and R<sub>4</sub> are alkyl groups and represent that a condition that a total of each number of carbons contained in R<sub>3</sub> and R<sub>4</sub>, and q and r is 34 is satisfied.)

### 3. Detailed Description of the Invention

#### (Technical Field of Industrial Application)

The present invention relates to novel diester of (meth)acrylic acid and the manufacturing method thereof. In further detail, it relates to a novel diester of

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(meth)acrylic acid, which can easily copolymerize with resins containing unsaturated groups under the existences of heat, ultraviolet rays, ionizing radiation, and a radical starter, and the manufacturing method thereof.

#### (Prior Art)

Conventionally, multifunctional (meth)acrylic esters, represented by trimethylolpropane tri(meth)acrylate, ethylene glycol di(meth)acrylate, pentaerythritol tri(meth)acrylate, and the like, have been regarded as

structural elements of so-called active energy beam curing resin compositions, such as ultraviolet-curing resin compositions and electron beam curing resin compositions, and are used as molecular weight regulators, crosslinking monomers, and the like in synthesizing various kinds of vinyl-based polymers.

Generally, multifunctional (meth)acrylic esters have a considerably strong stench, which is not so bad as monofunctional (meth)acrylic esters, and when they are used for print ink, coating material, and the like, they cause a problem to deteriorate working environment with the stench of unreacted monomers after curing. Moreover, since the multifunctional (meth)acrylic esters have high viscosity, even though they are used as diluents in the said use, their diluting effect is small, and thus they are necessarily used in a great amount to base polymers. As the result, the characteristics of base polymers decline, which may cause another defect, that is, resin composites to be prepared cannot show desirable performances in many cases.

Considering the actual circumstances, multifunctional (meth)acrylic esters, which resolve the said defects and can be suitably used as reactive diluents especially, have been gradually developed. However, as the actual situation, almost nothing that can satisfy all of reactivity, diluting

effect, skin stimulativeness, and the like is not recognized. Therefore, the development of novel multifunctional (meth)acrylic esters that can resolve the said defects is desirable in this industry.

(Problems to Be Solved by the Invention)

The present invention has an objective to provide novel multifunctional (meth)acrylic esters that are superior in reactivity and diluting effect, and can remarkably reduce skin stimulativeness.

(Means Used to Solve the Problems)

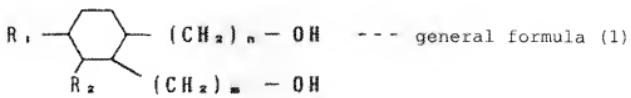
The present inventors have eagerly conducted examinations. As the result, they found that all said problems could be solved if bifunctional (meth)acrylic esters manufactured by being induced from specific glycol were used, and thus completed the present invention.

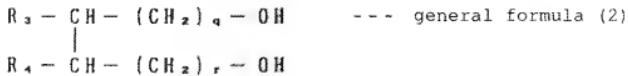
That is, the present invention relates to bifunctional (meth)acrylic ester, comprising dimer diol, manufactured by hydrogenating C<sub>36</sub> Dimer acid that is a dimer of high unsaturated fatty acid, and acrylic/methacrylic acid, both of which are esterified, and the manufacturing method.

In manufacturing the bifunctional (meth)acrylic ester as the present invention, it is necessary to use dimer diol as a raw material alcohol, manufactured by hydrogenating C<sub>36</sub> Dimer acid that is a dimer of high unsaturated fatty acid.

Here dimer acid refers to polymerized fatty acid, which mainly contains a dimer and is manufactured by polymerizing high fatty acid containing linoleric acid, such as sunflower oil, soybean oil, linseed oil, and tall oil by a publicly known method. To make dimer acid to dimer diol, a publicly known hydrogenating method can be adopted. Specifically, dimer diol can be prepared by using various kinds of hydrogeneous catalysts, such as Raney nickel, nickel diatomite, and inorganic fire-resistant substance (e.g., alumina and silica) to which a VIII group element in the regulated table of the elements, such as platinum, is supported and by using a normal catalytic reduction process. The conditions of hydrogenation are a range of temperature 60 to 250 °C or desirably 110 to 180 °C; under hydrogen pressure of normal pressure to 200 kg/cm or desirably 50 to 100 kg/cm; for 1 to 15 hours or desirably 4 to 8 hours.

A structural formula of dimer diol that can be prepared as mentioned above is hardly determined in one meaning. However, it contains at least one kind of glycol of the following general formula (1) and/or general formula (2) as a principal ingredient.





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(in the general formula (1), both  $R_1$  and  $R_2$  are alkyl groups and represent that a condition that a total of each number of carbons contained in  $R_1$  and  $R_2$ , and  $n$  and  $m$  is 28 is satisfied. Moreover, in the general formula (2), both  $R_3$  and  $R_4$  are alkyl groups and represent that a condition that a total of each number of carbons contained in  $R_3$  and  $R_4$ , and  $q$  and  $r$  is 34 is satisfied.)

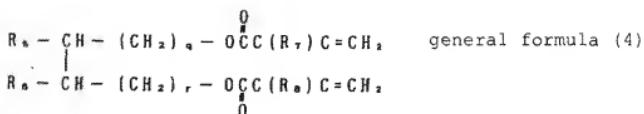
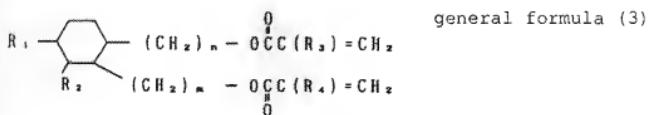
Glycol of the general formula (1) is an alicyclic compound, and glycol of the general formula (2) is one of aliphatic series. Both glycols commonly have two long-chain alkyl groups, no olefinic unsaturated bond, and a total of 36 carbons. Incidentally, the composition of dimer diol is usually that the weight ratio of glycol of the general formula (1) and glycol of the general formula (2) is about 6:4 to 8:2 although it depends on reaction conditions.

To prepare the bifunctional (meth)acrylic ester as the present invention by using the above-mentioned dimer diol, it is sufficient to conduct a usual esterification. If necessary, under the existences of a polymerization

inhibitor and an esterification catalyst, the said alcohol and (meth)acrylic acid can be dehydration-condensed. Here the reaction temperature is appropriately determined from the perspectives of reaction speed and prevention for secondary products from polymerized substances, and is normally in a range of 80 to 130 °C. The use amount of (meth)acrylic acid to dimer diol is more than a ratio in a chemical quantity theory, and the mol ratio is usually around 1.0 to 2.0 or desirably 1.1 to 1.5. The examples of the above-mentioned esterification catalyst include sulfuric acid, hydrogen fluoride, boron trifluoride, p-toluenesulfonic acid, and methanesulfonic acid. The range of the use amounts is usually about 1 to 10% by weight or desirably 2 to 5% by weight to the total use amount of (meth)acrylic acid and dimer diol. Moreover, the examples of polymerization inhibitor include hydroquinone, hydroquinone monomethyl ether, p-methoxyphenol, and phenothiazine, and the range of their desirable use amounts is usually 0.01 to 1% by weight to the total use amount of (meth)acrylic acid and dimer diol. Incidentally, to distill off water to be produced at esterification, if necessary, an azeotropic solvent, such as benzene, toluene, xylene, n-hexane, and cyclohexane, can be added.

The bifunctional (meth)acrylic ester as the present invention can be washed in water, alkaline aqueous solution, and the like or can also be refined through vacuum distillation, if necessary.

The bifunctional (meth)acrylic ester as the present invention that is prepared in these ways can be more specifically expressed by the following general formulas but is not limited to these general formulas.



(in the general formula (3), both R<sub>1</sub> and R<sub>2</sub> are alkyl groups and represent that a condition that a total of each number of carbons contained in R<sub>1</sub> and R<sub>2</sub>, and n and m is 28 is satisfied, and both R<sub>3</sub> and R<sub>4</sub> are hydrogen atoms or methyl groups. Moreover, in the general formula (4), both R<sub>5</sub> and R<sub>6</sub> are alkyl groups and represent that a condition that a total of each number of carbons contained in R<sub>5</sub> and R<sub>6</sub>, and q and r is 34 is satisfied, and both R<sub>5</sub> and R<sub>6</sub> are hydrogen atoms or methyl groups.)

The novel bifunctional (meth)acrylic ester as the present invention that is prepared as mentioned above can be easily copolymerized with various kinds of resins containing unsaturated groups, such as unsaturated polyester resin, epoxy acrylate resin, and urethane acrylate resin, under the existences of heat, ultraviolet rays, ionizing radiation, and a radical starter (photosensitizer) and thus can sufficiently show characteristics that these resins originally have.

(Examples)

The present invention is described in more specific referring to examples and application example below.

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However, the present invention is not limited to only these examples. Incidentally, % is based on a weight criterion unless mentioned specifically.

Example 1

974.6 g of dimer diol (manufactured by ARAKAWA CHEMICAL INDUSTRIES, LTD.; product name: "Dimer Diol XX-500"), 325.4 g of 98% acrylic acid, 1.95 g of methoxyphenol, 65.0 g of p-toluenesulfonic acid, and 520.0 g of cyclohexane were provided to a reaction equipment to which an agitator, thermometer, air blow tube, cooling pipe, and water separation tube were installed and were heated to

about 90 °C with blowing air under agitation. Then, while the water produced was removed out of the system through the water separation tube, esterification was conducted under agitation at the same temperature for five hours, and cooling was conducted when the amount of the water produced reached 70.6 g. The reacted fluid was dissolved in 700 g of toluene and was neutralized with 280.2 g of 20% aqueous solution of sodium hydroxide, and the water layer was separated and removed. Moreover, washing was conducted three times with 600 g of deionized water per once, then 0.464 g of methoxyphenol was added to distill the solvent off under vacuum, and thus 1,106.5 g of light yellow fluid was prepared. This fluid had the following characteristics.

Specific gravity (20 °C) 0.922

Viscosity (25 °C) 120 cps

Acid value 0.2 mgKOH/g

PII (Primary Irritation Index) 0.4

NMR analysis (in CDCl<sub>3</sub>): δ value (ppm)

6.40	vinyl proton	}	6H
6.12	vinyl proton		
5.82	vinyl proton		

4.15      ester adjacent proton    4H

1.75 to 0.80    aliphatic series proton    66.5H

IR analysis (neat):  $\nu$  (cm<sup>-1</sup>)

1728, 1636, 1188

Example 2

357.4 g of dimer diol, 142.6 g of 98% methacrylic acid, 0.75 g of methoxyphenol, 25.0 g of p-toluenesulfonic acid, and 425.0 g of cyclohexane were provided to the similar reaction equipment as the Example 1 and were heated to about 90 °C with blowing air under agitation. Then, while the water produced was removed out of the system through the water separation tube, esterification was conducted under agitation at the same temperature for five hours, and cooling was conducted when the amount of the water produced reached 23.7 g. The reacted fluid was dissolved in 300 g of cyclohexane and was neutralized with 120.5 g of 20% aqueous solution of sodium hydroxide, and the water layer was separated and removed. Moreover, washing was conducted three times with 300 g of deionized water per once, then 0.089 g of methoxyphenol was added to distill the solvent off under vacuum, and thus 413.2 g of light yellow fluid was prepared. This fluid had the following characteristics.

Specific gravity (20 °C) 0.916

Viscosity (25 °C) 125 cps

Acid value 0.3 mgKOH/g

PII

O

NMR analysis (in CDCL<sub>3</sub>): δ value (ppm)

6.10	vinyl proton	4H
5.55	vinyl proton	
4.14	ester adjacent proton	4H
1.94	methyl proton	6H
1.75 to 0.80	aliphatic series proton	66.5H

IR analysis (neat): ν (cm<sup>-1</sup>)

1721, 1640, 1165

Application Example (Evaluating film physical characteristics)

The bifunctional acrylic ester and the bifunctional methacrylic ester prepared in the Examples 1 and 2 were applied onto each hard glass plate with an applicator in a film thickness of 200 μm. Ultraviolet rays were radiated with one high pressure mercury arc (80 W/cm) by a radiation distance of 10 cm and a belt speed of 5 m/min. The film physical characteristics of peeled hardened coat prepared (width: 6 mm; length: 5 cm (chuck distance: 2.5 cm), film thickness: 200 μm) were evaluated. Table 1 shows the results.

Breaking elongation: an elongation rate to its own original length at pulling and breaking by a tensile rate of 50

mm/min.

Breaking strength: pulling by a tensile rate of 50  
mm/min. and a load was measured at  
breaking.

Modulus of elasticity: after pulling by 1 mm/min.,  
calculated on the basis of a  
slope of load - elongation curve  
at an elongation of 2.5%.

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	実施例 1 の硬 化皮膜	実施例 2 の硬 化皮膜
破断伸度 (%)	13.6	36.7
破断強度 (Kgf/cm <sup>2</sup> )	28.7	131.1
弾性率 (Kgf/mm <sup>2</sup> )	2.0	3.9

Table 1

	Cured film in Example 1	Cured film in Example 2
Breaking elongation (%)	(see the source)	
Breaking strength		

(Kgf/cm <sup>2</sup> )		
Modulus of elasticity		
(Kgf/mm <sup>2</sup> )		

(Effects of the Invention)

The bifunctional (meth)acrylic ester as the present invention is superior in any perspectives of polymerization reactivity, stench, and skin stimulativeness. Therefore, it can easily copolymerize with various kinds of unsaturated monomers or resins containing unsaturated groups under the existences of heat, ultraviolet rays, ionizing radiation, and a radical starter (photosensitizer) and thus can show an effect of availability for various uses as a useful multifunctional monomer. More specifically, the photocurable resin composition manufactured by using the bifunctional (meth)acrylic ester of the present invention as a reactive diluent makes cured film's flexibility, waterproofing, electrical insulation, and wetness to a base material satisfactory, and thus it can be suitably used as overprint varnishes, primary coating fluxes for optical fiber, overcoat agents for plastic including vinyl chloride, overcoat agents for metal, ink, coating materials, and the like.

Amendment (spontaneous)

September 4, 1990

To: Commissioner of the Patent Office

1. Description of the Present Case

1990 Patent Application No. 32999

2. Title of the Invention

Bifunctional (Meth)acrylic Ester and the Manufacturing  
Method Thereof

3. Person to Amend

Relationship to the case: Patent applicant

Address: 3-7, 1 Chome, Hirano Machi, Cyuo Ward, Osaka

Name: ARAKAWA CHEMICAL INDUSTRIES, LTD.

Phone: 06-939-2531

Representative: Shinobu Takahashi

4. Date of Amendment Order (Spontaneous)

5. Objects for the Amendment

(1) Column of "Claims for the Patent" in the  
Specification

(2) Column of "Detailed Description of the Invention"  
in the Specification

6. Contents of the Amendment

(1) Amend the "Claims for the Patent" in the  
Specification as "Amended Claims for the Patent"  
on the separate form shows.

- (2) Amend "regulated" on line 3, page 6 of the Specification to "periodic".
- (3) Amend "Kg/cm" on lines 7 and 8, page 6 of the Specification to "Kg/cm<sup>2</sup>".
- (4) Amend "28" on line 3, page 7 of the Specification to "30".

#### 7. Catalogue of the Attached Document

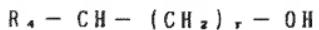
- (1) Amended Claims for the Patent 1

##### Amended Claims for the Patent

- 1) Bifunctional (meth)acrylic ester, comprising dimer diol, manufactured by hydrogenating C<sub>36</sub> Dimer acid that is a dimer of high unsaturated fatty acid, and acrylic/methacrylic acid, both of which are esterified.
- 2) A manufacturing method for bifunctional (meth)acrylic ester, which is manufactured by esterifying both dimer diol, manufactured by hydrogenating C<sub>36</sub> Dimer acid that is a dimer of high unsaturated fatty acid, and acrylic/methacrylic acid.
- 3) The manufacturing method, according to Claim 1) or 2), wherein the said dimer diol is a compound of the following general formula (1) and/or general formula (2).

R<sub>1</sub> - - - (CH<sub>2</sub>)<sub>n</sub> - OH --- general formula (1)

R<sub>2</sub> (CH<sub>2</sub>)<sub>m</sub> - OH



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(in the general formula (1), both  $R_1$  and  $R_2$  are alkyl groups and represent that a condition that a total of each number of carbons contained in  $R_1$  and  $R_2$ , and  $n$  and  $m$  is 30 is satisfied. Moreover, in the general formula (2), both  $R_3$  and  $R_4$  are alkyl groups and represent that a condition that a total of each number of carbons contained in  $R_3$  and  $R_4$ , and  $q$  and  $r$  is 34 is satisfied.)